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SPECTROSCOPY OF LASER IRRADIATED MIXTURES OF BORON TRICHLORIDE --ETC(U)
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SPECTROSCOPY OF LASER IRRADIATED MIXTURES OF BORON TRICHLORIDE AND HYDROGEN

U.S. ARMY MISSILE RESEARCH AND DEVELOPMENT COMMAND

Physical Sciences Directorate
Technology Laboratory

8 April 1977

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Preparation of missile propellants is one of the areas expected to be significantly impacted by laser induced chemistry. The synthesis by laser induced chemistry of specific boron compounds used as ingredients in propellants has been the purpose of our recent investigations.

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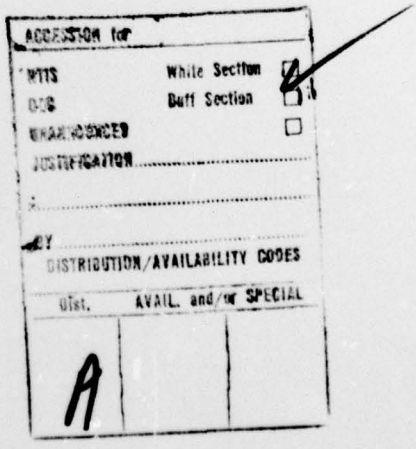

I. INTRODUCTION

Preparation of missile propellants is one of the areas expected to be significantly impacted by laser induced chemistry. The synthesis by laser induced chemistry of specific boron compounds used as ingredients in propellants has been the purpose of the recent investigations.

Initially mixtures of boron trichloride ($BC\ell_3$) and hydrogen have been irradiated by a pulsed CO_2 laser and the gas was observed [1,2] to emit a pale yellow luminescence. We have obtained the spectrum of this visible luminescence and identified spectral lines. Use of a Fourier transform IR spectrometer (FTS) enabled us to detect low level impurities in both the initial mixture of $BC\ell_3$ and H_2 and the reaction products. These IR spectra showed the presence of the impurity phosgene ($COC\ell_2$) in the initial gas mixture and CO in the reaction products in addition to the expected $HBC\ell_2$ and $HC\ell$.

II. EXPERIMENTAL

Typically, a 10-cm brass or stainless steel cell fitted with 5 cm diameter $NaC\ell$ or KBr windows was used. Three of those cells can be seen in the upper middle part of Figure 1. It was passivated for several hours with $BC\ell_3$ then evacuated and refilled with 25 to 100 Torr of $BC\ell_3$ and 25 to 400 Torr of H_2 in a desired ratio. This mixture was irradiated with 200 ns wide 0.7 J pulses from a Lumonics Model TEA 203 tunable multigas laser operating with a 2-second repetition rate at the P20 CO_2 (10.591 μm) wavelength. During irradiation, visible luminescence was detected through a window in the cell perpendicular to the beam direction and recorded on Polaroid type 107 film after passing through a prism spectrograph. Absorption spectra were determined with a Digilab Model 20-B Fourier transform spectrometer before and after irradiation. This instrument is shown in Figure 2.

III. TECHNIQUE FOR IDENTIFYING LUMINESCENCE SPECTRA

A quick and accurate method for identifying optical spectra has been developed. In this technique, positions corresponding to given wavelengths are measured from an arbitrarily chosen reference line on a spectrographic plate of known wavelengths taken with our prism spectrograph. These distances and wavelengths are used to calculate the coefficients of a polynomial using a least-squares fit. We use a basic program for polynomial regression of any desired degree up to 9th degree written for the 9830A Hewlett-Packard programmable calculator for this fit. This polynomial is then used to plot a curve of linear distance versus wavelength. This step completes the calibration.

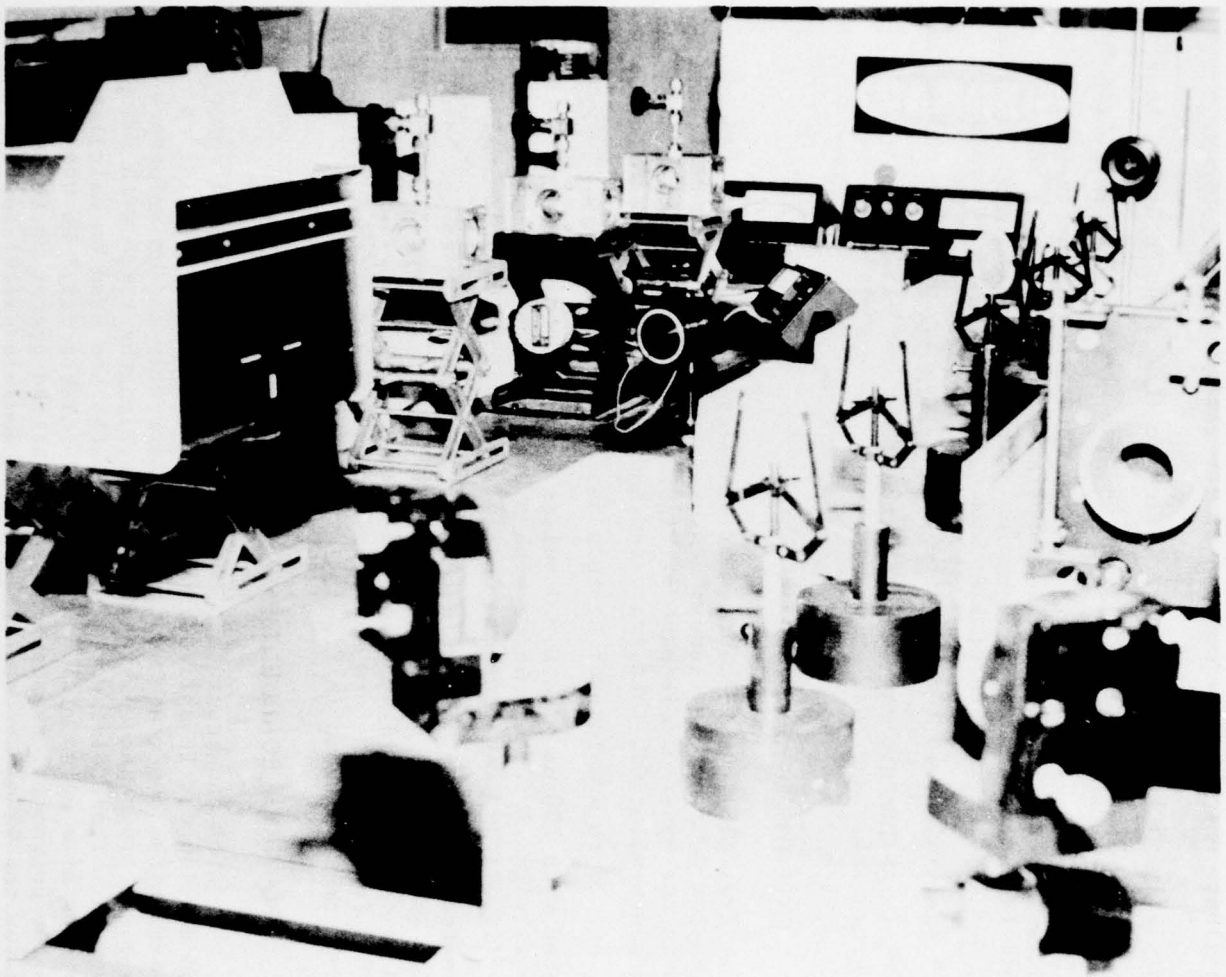

Figure 1. Gas cells for laser irradiation.

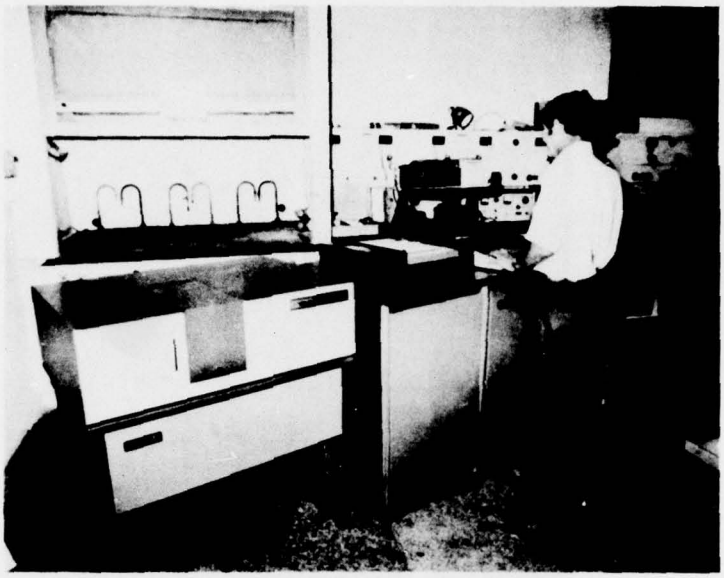

Figure 2. Fourier transform spectrometer.

The calculator will then plot, in our particular spectrographic plate format, the position of any wavelength programmed into it. These calculated spectra are plotted as a column of lines of given equal horizontal length and vertical separation calculated from the polynomial obtained from the calibration points.

Identification of molecular and atomic spectra from a spectrographic plate of an unknown is made by overlapping it with calculator drawn spectra plotted on a transparency. Speed and accuracy are increased over conventional methods since several spectral lines of a series can be simultaneously compared, thereby eliminating the usual tedious method of measuring the position of each line individually. Deviations between data and standard spectral line positions, usually due to the geometry of a particular experimental arrangement or to the mode of excitation, can be evaluated immediately by inspection. In this manner, confusion arising between measured and standard spectra is reduced. Relative intensity in addition to wavelength can be indicated on the calculator plot. This is illustrated in the flame spectrum of boron (Figure 3). The principal limitation of this method is the availability of known spectra.

IV. RESULTS

The absorption spectrum after a 300-pulse irradiation of a 50-Torr mixture of boron trichloride and hydrogen in a 1:1 ratio is shown in Figure 4. An increase in $HC\ell$ absorption band after irradiation can be seen at 2900 cm^{-1}, accompanied by a decrease of $BC\ell_3$ absorption

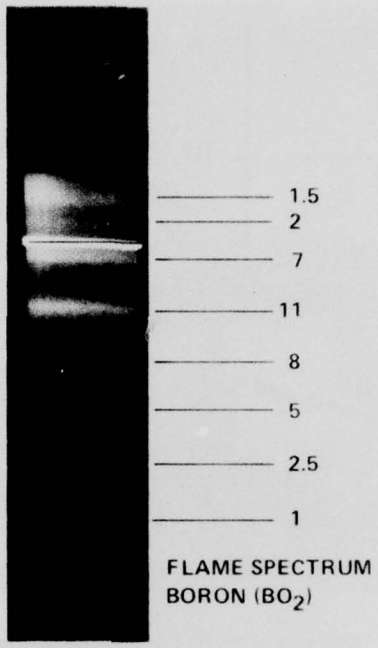

Figure 3. Flame spectrum of boron compared with computed spectrum.

at 1400, 995, and 955 cm^{-1}. Creation of bands at 2620, 1090, and 900 cm^{-1} shows that $HBC\ell_2$ was formed as an end product of laser induced reactions according to the reaction

$$BC\ell_3 + H_2 + h\nu \rightarrow HBC\ell_2 + HC\ell$$

as previously reported by Rockwood and Hudson [1]. Subsequently the optimum starting ratio of $BC\ell_3/H_2$ was found to be 1:4 for $HBC\ell_2$ formation. The optical emission spectra of $BC\ell_3$ irradiated with a pulsed CO_2 laser was found to have a continuous spectral distribution [3,4] from 5300 Å to > 6300 Å. When a mixture of $BC\ell_3$ with an excess of H_2 was used emission band spectra which fit the $B^1\Sigma \rightarrow A^1\Pi$ and $d^3\pi \rightarrow a^3\pi$ series of CO were observed. Bands due to $C\ell^+$ and $C\ell_2^+$ overlapped by the two most prominent bands of the $^3\pi \rightarrow {}^3\pi$ series of C_2 were detected as shown in Figure 5. $COC\ell_2$, a main impurity in the c.p. grade $BC\ell_3$ used, was identified as the probable source of CO. There were also bands just above 5000 Å which correspond to BO bands previously observed [5].

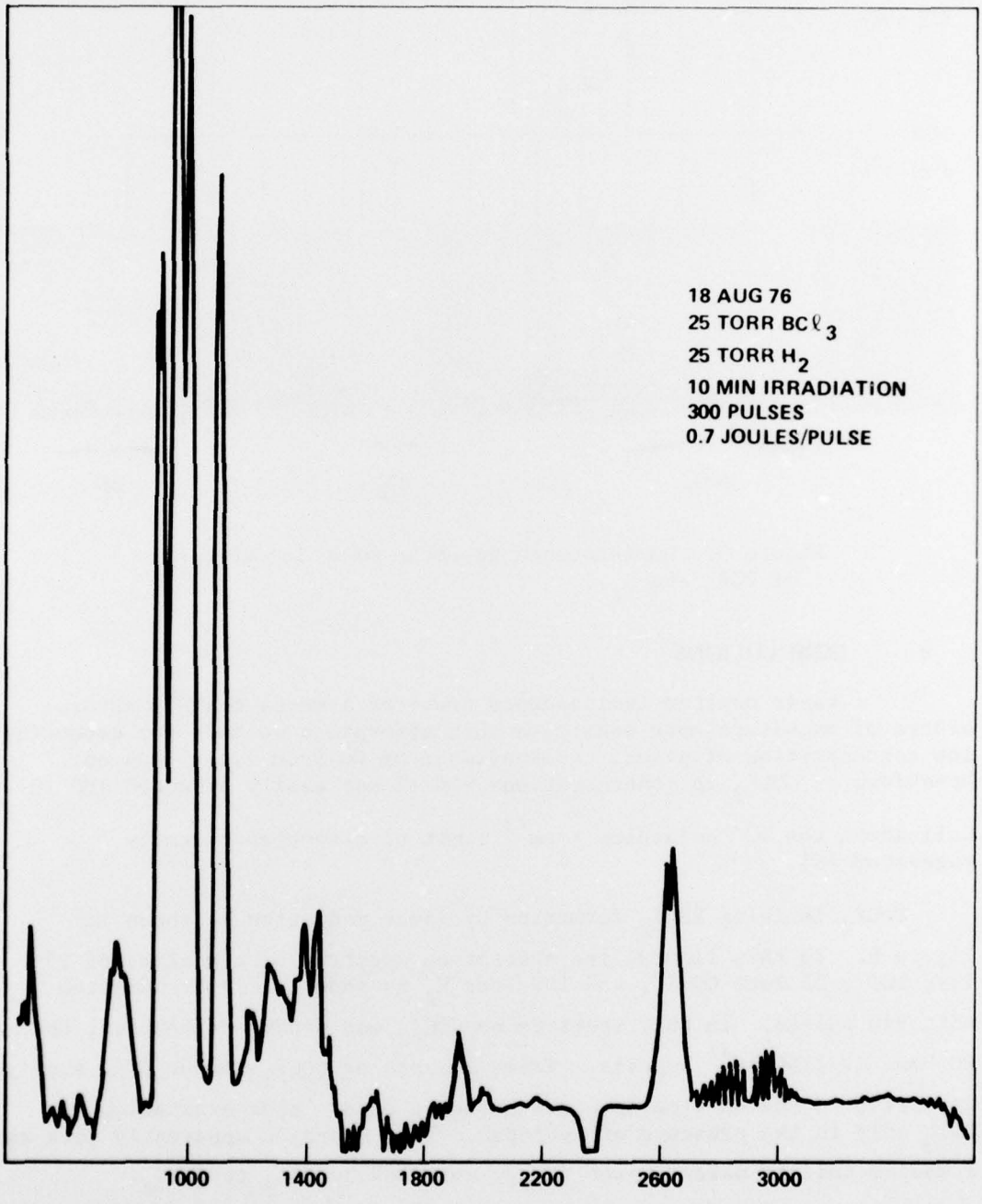

Figure 4. Absorption spectrum of a 50 Torr mixture of $BC\ell_3$ and H_2 in a 1:1 ratio, after irradiation with 300 pulses.

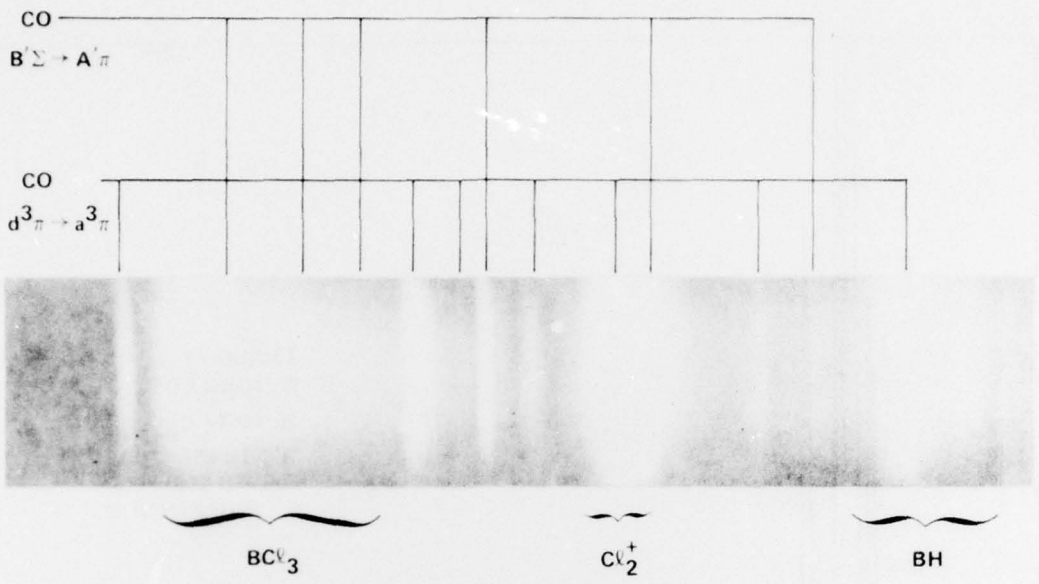

Figure 5. Luminescence spectrum of a 1:4 mixture of $BC\ell_3$ and H_2.

V. CONCLUSIONS

Laser excited luminescence provides a means that is several orders of magnitude more sensitive than absorption methods for detecting low concentration of gases. Luminescence of CO from laser induced breakdown of $COC\ell_2$ in concentrations ~ 0.1% was easily detected and is well above the 10^5 molecules · cm^{-3} limit of detection recently suggested [6].

$COC\ell_2$ inhibits $HBC\ell_2$ formation by laser radiation as shown in Figure 6. In this figure, the absorption spectrum of a mixture of 25 Torr $BC\ell_3$, 25 Torr $COC\ell_2$, and 100 Torr H_2 is shown after irradiation with 810 pulses. In this spectrum no $HBC\ell_2$ was produced; however, the CO band at 2150 cm^{-1} appears. Trace amounts of $COC\ell_2$ in our $BC\ell_3$ supply gave rise to the CO line spectrum observed under laser excitation of $BC\ell_3$ only in the presence of hydrogen. Thus hydrogen apparently acts as a medium that transfers laser energy absorbed by $BC\ell_3$ to $COC\ell_2$.

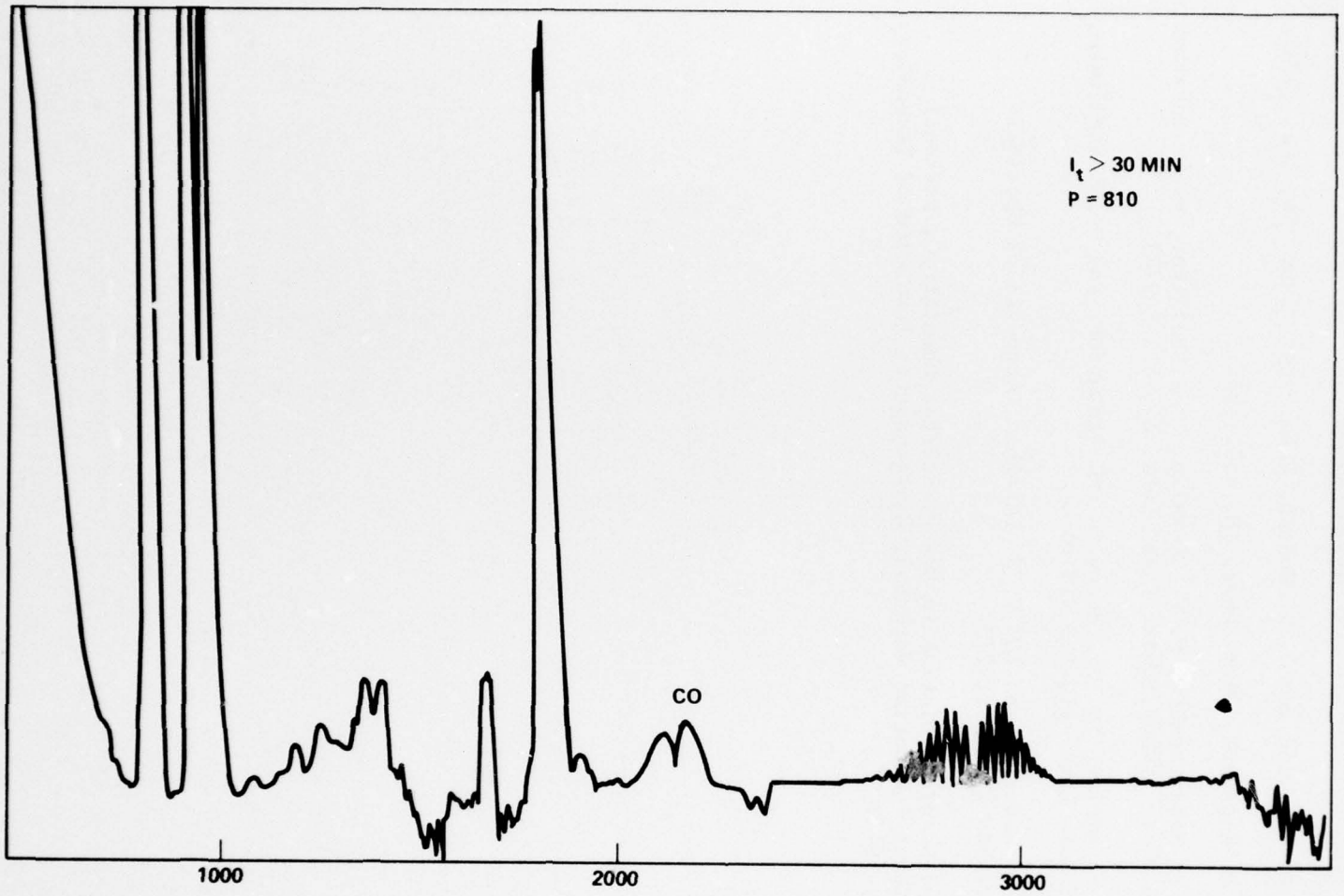

Figure 6. Absorption spectrum of a mixture of 25 Torr $BC\ell_3$, 25 Torr $COC\ell_2$, and 100 Torr H_2 after irradiation with 810 pulses.

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